



Catalyst layer optimization by surface tension control during ink formulation of membrane electrode assemblies in proton exchange membrane fuel cell

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ARTICLE INFO

Article history:

Received 10 November 2010

Received in revised form

21 December 2010

Accepted 4 January 2011

Available online 13 January 2011

Keywords:

Membrane electrode assembly

Catalytic layer

Ink composition

Sieve printing

Surface tension

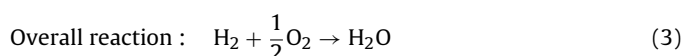
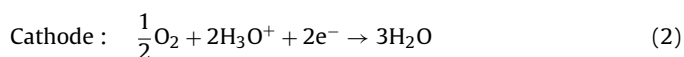
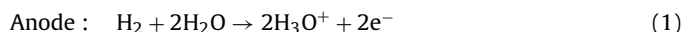
ABSTRACT

A cost effective production of the membrane electrode assemblies (MEA) is a crucial issue for the generation of electricity by proton exchange membrane fuel cells (PEMFC). The deposition of the exact catalyst content on the electrodes in a single printing step is desirable to save processing time and enable cost reduction. In this study, an innovative MEA production process by screen print is developed to produce high performance catalyst layers. The control of the surface tension of the catalyst ink is fundamental to allow the catalyst layer deposition in a single printing step. The electrodes prepared in this way show higher performance than those prepared in several steps. The optimal ink developed shows a viscosity of 2.75 Pa s, a total solid content of 33.76 wt.%, a density of 1.294 g cm⁻³, and tack value of 92 U.T.

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1. Introduction

The development of systems capable of generating electricity from hydrogen is considered an important step to ensure the power supply in the coming years [1]. Fuel cells are devices capable of generating direct current and heat from the chemical energy of a fuel and an oxidizer [2]. Among the various types of fuel cells, those that use a proton exchange membrane (PEMFC) as electrolyte have characteristics that make their use feasible for portable, stationary, and automotive applications [1,2]. In a PEMFC system supplied with hydrogen and oxygen, two electrochemical reactions take place at the electrodes, which are separated by a polymer electrolyte: the production of water as an overall reaction product and the highly efficient generation of electricity and heat. The partial and overall reactions to hydrogen and oxygen are shown in Eqs. (1)–(3), respectively [2,3]:



In a PEMFC the reactions occur in the membrane electrode assembly (MEA), which involves a polymeric membrane faced with two gas diffusion electrodes (GDE), the anode, and the cathode. Each GDE is composed of a catalyst layer and a gas diffusing layer (GDL) [2,3].

The catalyst layers of the electrodes are formed by a mixture of catalyst and ionomers of the electrolyte material, such as Nafion[®], with structural porosity for the diffusion of both reactants and products. The catalyst plays the role of speeding up the oxidation and reduction reactions that occur at the anode and cathode, respectively. The Nafion[®] ionomer provides a pathway for the protons that were formed in the catalytic sites across the electrode in order to ensure optimal conditions for anodic and cathode reactions to generate electrical current [2,3]. The GDL promotes a uniform distribution of reactant gases over the catalyst layer and conducts the electrons generated in the catalyst layer anode reaction to the external circuit [2–4].

1.1. Membrane electrode assembly preparation

Several MEA preparation techniques have been studied [4–9] with the formulation of a precursor ink of catalyst layer (PCL) in order to increase cell performance and reduce overall costs. Nafion solvents and alcohols are generally mixed with catalyst and other components for the PCL preparation [6,10–14]. However, due to the high volatility of commonly used solvents, the ink and, consequently, both the stability and

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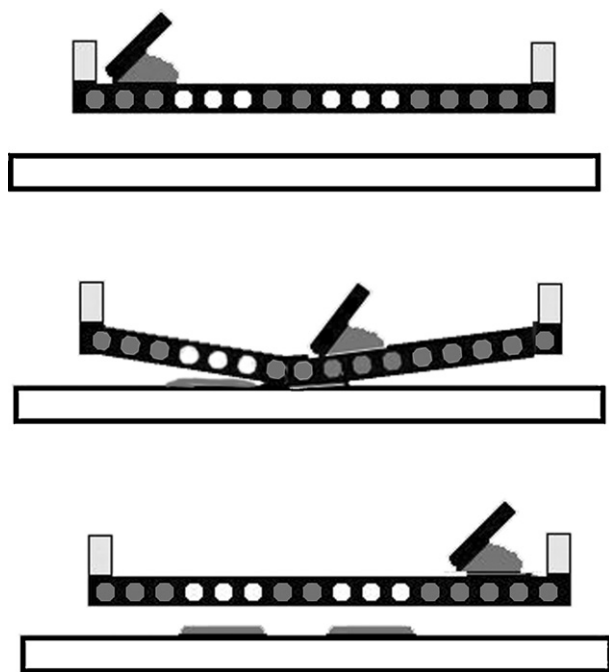


Fig. 1. Schematic cartoon of the screen print process scheme before, during and after printing.

reproducibility of the MEA fabrication process are difficult to guarantee.

1.2. Screen print process

The screen print process consists of forcing an ink across a print matrix and being deposited on the desired surface [15]. Fig. 1 shows a schematic illustration of the main steps involved in the screen print process.

Each screen used in the screen print matrix preparation has a free volume between the wires. The printing ink penetrates the free volume and is then transferred to the printing substrate [15].

1.2.1. Precursor ink of the catalyst layer

The preparation of the precursor ink of the catalyst layer (PICL) consists of a dispersion of different components in a suitable vehicle. The ink must provide an easy application, and the deposits must be uniform and stable over time. After drying, the ink vehicle must be completely eliminated, and the layer applied must have electronic and protonic conductivity [2,4–6,16].

The solvent must surround the solid ink components and keep them dispersed, allowing the ink application through known processes [16]. The solvent is the first ink component to come in contact with the surface on which the ink is applied. Thus, the solvent surface tension determines the ink surface tension. The correct ink surface tension must be lowest than the printing substrate surface tension in order to avoid problems of wetting and adhesion, as well as to prevent coating failures [16].

When liquids with different surface tensions are mixed, the resulting surface tension generally is close to the lowest one because the liquid surface is enriched with a larger amount of fluid that containing the lowest surface tension [16]. The liquid surface tension can be determined directly by appropriate tensiometers for each different liquid system. For solids (print substrates) the surface tension measurement can be taken indirectly by applying a variety of solutions with progressively higher surface tensions in a print substrate and checking for a wet behavior change. When the solution surface tension becomes equal to that of the print substrate,

Table 1

Vapor pressure of some common solvents [17].

Solvents	Vapor pressure (mm Hg at 20 °C)
Ethylene glycol	0.08
1-Heptanol	0.50
2-Propanol	33.0
Ethanol	44.6
Methanol	96.0

wettability problems start to occur, and the solution surface tension value must be considered that of the substrate surface tension [16].

Depending on vapor pressure, a solvent might have a higher or lower volatility at any temperature, which results in different ink drying times by solvent evaporation. The lower the vapor pressure, the less volatile the solvent will be, with a longer drying time by evaporation being required [16]. Table 1 shows the vapor pressure of some common solvents [17].

The solid content consists of the non-volatile ink components that remain after drying. Similarly, the weight fraction of the solvent is determined by the amount of volatile material that is removed from the ink in the drying process. Both contents (solids and solvent) must be well-controlled and corrected, if necessary, at the end of the ink preparation process [16]. The maximum amount of solids in an ink is determined by the critical concentration of particles per volume (CCPV). This is defined as the maximum concentration of solid particles related to the ink weight in which the vehicle is able to fill all the gaps around the particles. Below this concentration, i.e. with vehicle excess, there is a mixture behavior change that determines ink features and allows application in the printing process [16]. In addition to solids and solvent determinations, an ink must also be characterized by other properties, such as density, viscosity, and tack value [16,18].

The tack value (a dimensionless number) is a measure of the internal resistance that the layers of a fluid present against separation. This feature can interfere with the ink performance during the application step [18].

In this study a stable precursor ink of catalyst layer with adequate surface tension for application on GDL was formulated, and an application process of the exact solid content by screen print was developed, allowing for the use of adequately prepared gas diffusion electrodes in the manufacturing of MEAs for PEMFC.

2. Experimental

An ideal MEA production process should be reproductive, fast, able to increase in scale, and stable over time. Based on the application of $0.4 \text{ mg Pt cm}^{-2}$ at the anode, the precursor ink of catalyst layer was formulated by calculating the mass of solids to deposit for each electrode, using the adequate relationship between solids and solvents (CCPV) and searching the adequate solvent.

The catalyst employed was a platinum 20 wt.% supported on carbon black (Pt/C) manufactured by BASF Company. The Nafion ionomer was obtained from a Dupont SE-10072 solution. The catalyst and Nafion ionomer ratio used was 65:35 [6], resulting in 2 mg cm^{-2} of catalyst and 1.077 mg cm^{-2} of Nafion.

To select the correct screen to print matrix preparation, the free volume between the wires of the screen was calculated and reported in billions of cubic microns per square centimeter (BCM cm^{-2}). The calculation was made from the diameter of the wires and the number of wires per linear centimeter ($l \text{ cm}^{-1}$), which is also known as “screen ruling”.

The density and solids content of the Nafion SE-10072 solution were determined by the ratio between mass, before and after the drying process, and between known mass and volume, respectively.

With this information the theoretical density of the Nafion ionomer was calculated by linear extrapolation. The theoretical density of the catalyst Pt/C was also calculated through the weighted average of the weight and densities of platinum and carbon Vulcan XC72 present on it. The needed weight of these components per square centimeter of electrode was then converted to volume by means of their densities.

The CCPV was determined by weight by adding and mixing small amounts of solvent to solids (dry mixture of catalyst and Nafion) and looking for an ink behavior transition when solvent excess was reached [16]. A solvent or solvent mixture capable of maintaining all ink components evenly dispersed, so as not to evaporate at room temperature due to its low vapor pressure, was chosen to be used as a PICL vehicle. A first ink labeled “PICL1” was prepared using ethylene glycol as vehicle, Nafion® ionomer from DuPont™ solution SE-10072 and catalyst Pt/C. These reactants were mixed and dispersed in a beaker with 12,000 and 3000 rpm for 15 min. The dispersion was then subjected to heating and magnetic stirring to remove the solvents of the Nafion solution by evaporation, resulting in the ink which was ready to print. A second ink labeled “PICL2” was prepared using a modified solvent with 5 wt.% of 1-heptanol added to ethylene glycol in order to maintain the same ink solids level at the end of the process.

The electrodes were prepared by applying the inks prepared (PICL1 and PICL2) through screen print (E1 machine from EKRA Company) on the gas diffusion layer (Electrode Backing EC-CC1-060T from the ElectroChem Company). The MEAs were prepared by hot pressing [6] of the electrodes on both sides of previously treated Dupont™ Nafion 115 membranes [4,6]. The MEAs were evaluated in a single cell of 25 cm² from Electrocell, after 3.5 h of activation [5], when the potential versus current density curves were obtained for polarization evaluation of MEAs [4,6,19]. In this study, the potential was measured between 1.0 and 0.3 V [6,19–21]. The unit cell was operated at 75 °C. The anode was supplied with analytical hydrogen at 90 °C with a flow of 355 mL min⁻¹, and the cathode was supplied with analytical oxygen at 80 °C with a flow of 178 mL min⁻¹. In both the cathode and the anode, the reactive gases were saturated with high pure water vapor and supplied with 1 bar of absolute pressure.

The solvents and carbon cloth surface tension were determined using a KRÜSS K8551 tensiometer (ring method). The microstructural evaluation was performed by scanning electron microscopy (SEM) Philips XL 30. The solids content of the inks was experimentally determined by mass difference between samples placed on a watch glass before and after drying at 120 °C. The ink densities were calculated by weighted average and experimentally determined by the relationship between volume and mass of ink samples. The ink viscosity was determined using a Laray viscometer. The ink tacks were determined in a Tack-O-Scope BV MAV/EL100 from Test Print Company.

3. Results and discussion

The volume of commercially available screen with different rulings was evaluated, as shown in Table 2.

Table 2
Relationship between screen ruling and the volume of commercial screens.

Screen ruling lines per centimeter ($l\text{ cm}^{-1}$)	Measured volume (BCM cm^{-2})
15	27.2
32	12.6
50	7.17
77	5.24
120	2.24

The CCPV of Nafion and catalyst mixture in ethylene glycol was found to be 34.1 wt.%. Thus, to deposit all PICL in a single printing step, the mass of solids and solvent to be applied per square centimeter of electrode was calculated to 0.4 mg Pt cm⁻² at each electrode, which corresponds to 3.077 mg of the Nafion/catalyst mixture at the proportion of 35:65. According to the estimated CCPV, the minimum mass of ethylene glycol per square centimeter of electrode was found to be 5.949 g. Furthermore, the minimum amount of ethylene glycol ($d = 1.036\text{ g cm}^{-3}$) to be applied per square centimeter of electrode was calculated to be 0.005742 cm⁻³ (5.742 BCM).

The density and solids content of Nafion® SE-10072 aqueous solution were 1.071 g cm⁻³ and 11.37 wt.%, respectively. From the linear extrapolation of these values (and the water density), the Nafion ionomer density value of 1.120 g cm⁻³ was estimated. The apparent density calculated for the catalyst was 4.415 g cm⁻³. Using Nafion and catalyst estimated mass and densities were calculated (in the ratio 35:65), the solid masses to be applied per square centimeter achieved 1.415 BCM cm⁻², which indicate that the sieve must have had a minimum volume of 7.157 BCM cm⁻². Based on the available sieve volume, a sieve of 7.17 BCM cm⁻² was selected for the screen print matrix preparation, and the solvent content was corrected for this volume.

Based on data shown in Table 2, the printing process should have provided the pre-calculated catalyst mass deposition on carbon cloth in a single application of the PICL1. However, the carbon cloth showed low wettability by the PICL1, and the mass deposited, determined after drying, was much lower than calculated. From these observations the carbon cloth, ethylene glycol, and other solvents that could be used as additives for adjusting the surface tension of the ink were experimentally evaluated. The carbon cloth surface tension value was 32.5 d cm⁻¹. Some solvents surface tension values are presented in Table 3.

According to theory [16] the ink surface tension must be lower than the printing substrate surface tension in order to allow an adequate wetting during printing. Thus, among the solvents with surface tension below 32.5 d cm⁻¹, 1-heptanol was chosen to be used in the PICL2 formulation because of its low vapor pressure. By carrying out systematic experiments of mixing progressively increased amounts of 1-heptanol on ethylene glycol, an optimum weight fraction of 5% was found to be sufficient to produce an adequate ink vehicle, with suitable surface tension for application on carbon cloth.

Printing with the PICL1 demanded four repetitions of the printing step. Using the same conditions, printing with PICL2 succeeded in depositing all catalyst (0.4 mg Pt cm⁻²) in only one printing (deposition) step. Such features led to the conclusion that the surface tension adjustment was essential to overcome the low compatibility observed between the carbon cloth and the PICL1.

Another important parameter for the optimized fabrication of MEAs is the printing speed. The mass increase dependence on the printing speed was determined experimentally and is displayed in Fig. 2.

The data shown in Fig. 2 evidenced that the speed reduction from 110 to 50 mm min⁻¹ causes an increase of 29% in the mass transfer (using PICL2). Since the anodes (0.4 mg Pt cm⁻²) were

Table 3
Experimental surface tension of some solvents.

Solvent	Surface tension ($d\text{ cm}^{-1}$)
n-Hexane	18.8
Ethanol	26.8
1-Heptanol	27.6
Ethylene glycol	43.0
High pure water	71.5

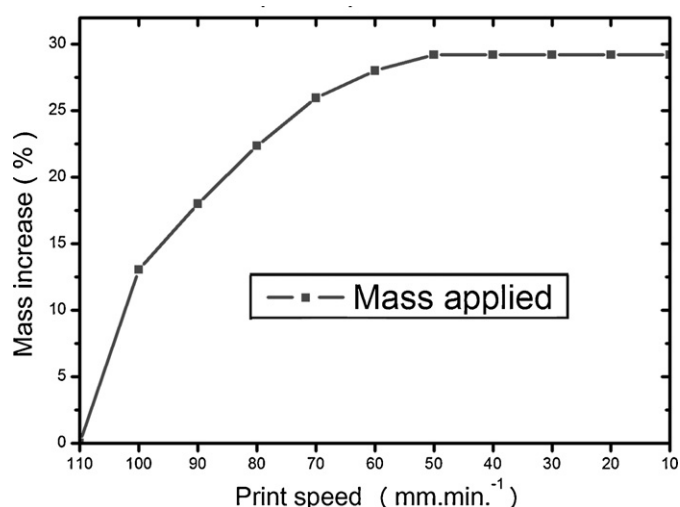


Fig. 2. Mass transfer dependency on the printing speed.

already printed with 110 mm min^{-1} and 1.6 bar, a speed reduction to 50 mm min^{-1} showed catalyst mass increasing up to $0.52 \text{ mg Pt cm}^{-2}$, as expected. Other experiments with increasing print pressure at the same speed allowed the deposition of $0.6 \text{ mg Pt cm}^{-2}$ in only one print step with 1.73 bar.

Thus, anodes and cathodes printed with the PICL2 formulation in only one print step per electrode were tested in single cell operation. Fig. 3 shows single cell performances of MEA 1 and MEA 2, using PICL1 and PICL2, respectively.

The polarization curves in Fig. 3 show that current densities at 600 mV of 568 and 712 mA cm^{-2} were achieved with MEA 1 and MEA 2, respectively. The experimental data indicated the MEA prepared with PICL1, using 3 and 4 printing steps for anodes and cathodes, respectively, exhibited lower performance than the MEA prepared with PICL2, using one printing step per electrode. Figs. 4 and 5 show MEA 1 and MEA 2 micrographs, respectively, in which the lower parts of the picture are the catalyst layers of the MEAs and the upper parts the polymeric membranes.

In Fig. 4 cracks can be observed throughout the catalyst layer, which may be related to a decrease in performance, given that the proton conductivity depends on structural integrity. It is expected that the repetition of several printing steps results in cracks on electrode structure due to the poor adhesion between PICL1 and carbon

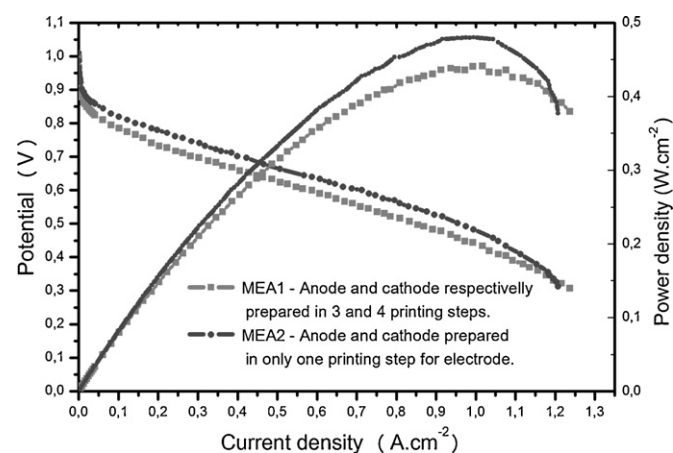


Fig. 3. Polarization curves of MEAs 1 and 2. Electrode surface area: 25 cm^2 , 1 atm, PEMFC single cell at 75°C , Anode $0.4 \text{ mg Pt cm}^{-2}$ with H_2 355 mL min^{-1} at 90°C , Cathode $0.6 \text{ mg Pt cm}^{-2}$ with O_2 178 mL min^{-1} at 80°C . Both reactive gases saturated with high pure water.

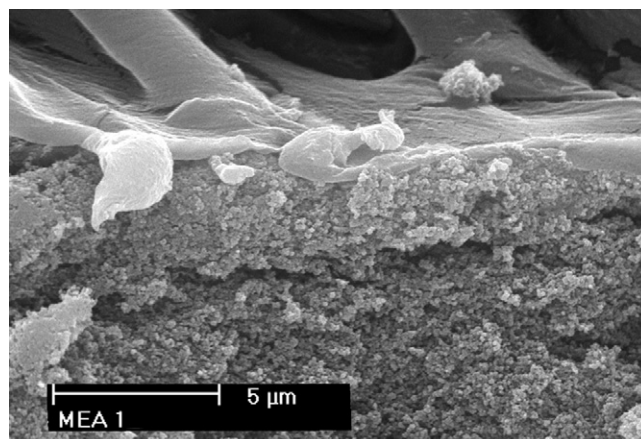


Fig. 4. Micrograph of MEA 1 printed with the PICL1 using several print steps.

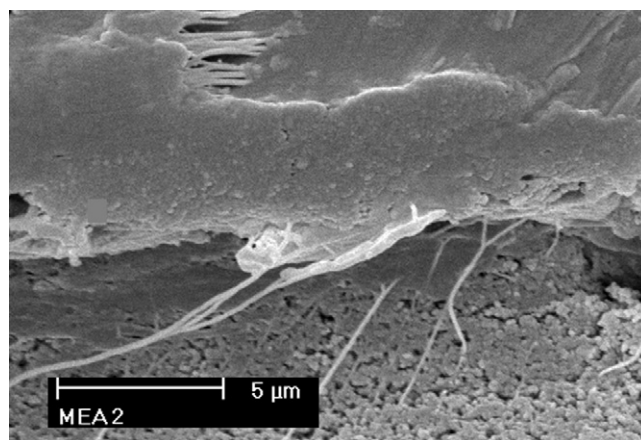


Fig. 5. Micrograph of MEA 2 printed with the PICL2 in only one print step.

cloth. The repetition of the printing steps is likely to contribute to the formation of cracks in previously applied layers. In Fig. 5 the MEA produced using PICL2 was more homogeneous than that of Fig. 4. This effect may be attributed to the adequate ink surface tension, which enabled the implementation of the mass required in only one print step. This prevents the catalyst layer from being subjected to further stress, thus ensuring its integrity and resulting in higher MEA performance, as shown in Fig. 3. Another observed effect was the ink penetration into the GDL. Figs. 6 and 7 show micrographs of MEA 1 and MEA 2.

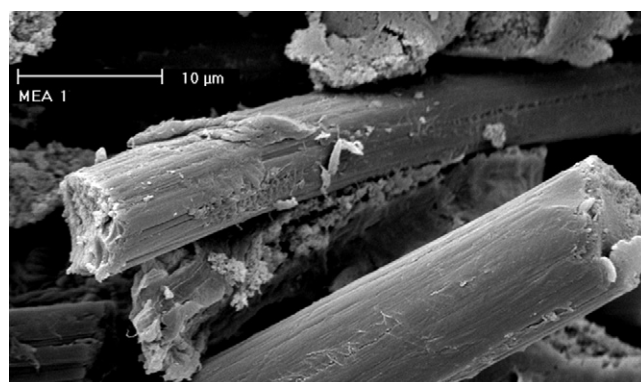


Fig. 6. MEA 1 GDL printed with PICL1, ink without surface tension adjustment.

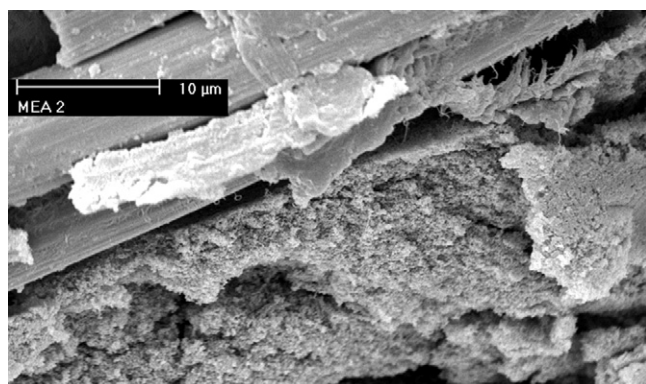


Fig. 7. MEA 2 GDL printed with PICL2, ink with surface tension adjustment.

Table 4

Precursor inks of catalyst layer solid contents.

Ink	Solid contents (wt.%)		Error %
	Experimental	Calculated	
PICL1	34.04	33.27	2.31
PICL2	33.79	33.16	1.90

Table 5

Precursor inks of catalyst layer densities.

Ink	Density (g cm ⁻³)		Error (%)
	Experimental	Calculated	
PICL1	1.262	1.306	3.37
PICL2	1.270	1.294	1.89

A better penetration of PICL2 in MEA 2 GDL can be observed in Fig. 7, as compared to PICL1 in the MEA 1 GDL. This confirms the efficiency of the surface tension adjustment.

After ink preparation, the effective ink solid content and density were carefully checked. Such values are shown in Tables 4 and 5, respectively. The small differences between the calculated and measured values of solid content suggest that the mixing and heating procedures used for ink preparation are adequate.

As expected, both inks have practically the same densities, indicating that the Nafion ionomer and the catalyst densities were accurately determined.

In order to verify whether or not the inks have suitable characteristics for screen print application, their viscosities were determined and compared with a commercial screen print ink. The results are shown in Table 6.

According to Table 6, the formulated ink viscosities were suitable for the application process since the values are very similar to those of the commercial ink. The tack value, shown in Fig. 8, was performed to verify the ink behavior on the screen print machine and to compare its stability in relation to a commercial screen print ink.

The tack values determined at the initial time ($t = 0$) were 55 U.T. and 92 U.T. for commercial screen print ink and PICLs (PICL1 and PICL2), respectively. The tack value is dimensionless and ranges from 0 to 600 in the equipment used. The PICLs have a higher

Table 6

Commercial and formulated precursor inks of catalyst layer viscosities.

Ink	Viscosity (Pa s)
Commercial	2.92
PICL1	2.73
PICL2	2.75

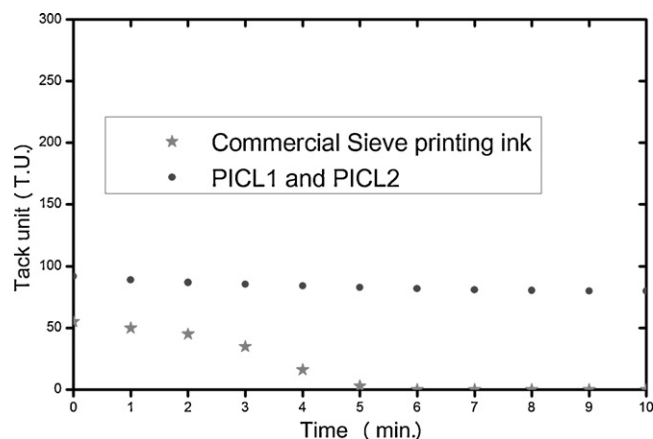


Fig. 8. Time dependence of tack value of commercial and formulated inks.

resistance to separating on layers than does the commercial ink, thus indicating that the PICLs hardly run across the screen before or after electrodes printing. Consequently, their use will require higher pressures than those required for commercial ones. This behavior has been observed in screen printing tests with different applied pressures. Another important observation from Fig. 8 is the progressive decrease of the tack of commercial screen print ink, reaching zero after 6 min. Such a feature is possibly associated with solvent evaporation during the experiment. Since the tack values of the PICLs did not change significantly over time, no solvent evaporation or other losses occurred. Such properties ensured that the solid contents of the PICLs show no significant changes over time, further evidencing the stability of the developed ink.

4. Conclusions

An adequate match between the surface tension of the ink and the carbon support was found to be essential to prepare a precursor ink of catalyst layer efficient for the fabrication of MEAs for PEMFC by screen print process.

The ink types and printing process variables studied allowed for the preparation of MEA cathodes and anodes of PEMFC, with catalyst loads of 0.6 and 0.4 mg Pt cm⁻², respectively, with the same screen print matrix and the same ink as proposed. The screen print system could be adjusted to an adequate application of the precursor ink of catalyst layer in only one printing step per electrode, thus reducing process time and cost and enhancing stability.

The developed precursor ink of the catalyst layer (PICL2) has all the necessary features for the screen print application process. The use of an appropriate ink with one screen print process step is innovative, faster, and more reproducible than those reported in the literature, thus allowing for a more efficient MEA production.

Acknowledgements

To the Energy and Nuclear Research Institute – IPEN and to SENAI Theobaldo de Nigris School, both located in São Paulo, Brazil. To the National Council for Scientific and Technological Development – CNPq – for financial support. Thanks are also due to M.C. Jacome for the use of the laboratory of ink characterization.

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